

Kinetic Study of Oxidation of Acetyl Acetone by Nicotinium Dichromate

S.K. NIGAM[#], PRIYANKA PATEL^{*}, AKS TIWARI[#] and ANITA TIWARI[#]

^{*}Guest Lecturer,

Govt. Tilak PG College, Katni, M.P., INDIA.

[#]Assistant Professor,

Govt. Model Science College, Rewa, M.P., INDIA.

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ABSTRACT

The oxidation of active methylene group has been carried out with Nicotinium dichromate (3-carboxy pyridium, NDC) in acetic acid medium in the presence of H^+ ion. It is found that rate is a direct function of first power concentration of oxidant i.e. NDC and zero order with respect to substrate i.e. active methylene compound. The reaction was found to increase with increase. concentration of acid. The reactive species is H_2CrO_4 .

Keywords: Oxidimetric, Degradation, Nicotinium dichromate.

INTRODUCTION

Nicotinium dichromate (3-carboxy pyridium NDC) is a titrant for the oxidimetric determination of some typical active methylene compound in acidic medium. This chromium (VI) complex of heterocyclic bases is a mild oxidant, soluble in organic solvent and used under anhydrous condition¹. It is a new oxidant, non-hygroscopic, non-photosensitive stable yellow orange solid². Kinetic and mechanistic studies of oxidation by chromium (VI) complexes like PFC, QFC PCC, QCC, BPCC, PBC, and BPC are common and the oxidation is first order with

respect to chromium (VI) reagent and is catalyzed by mineral acid.

While the oxidation of active methylene compound by NDC is very rare and scanty and none of the researcher acclaimed the use of NDC in probing the oxidation kinetics of active methylene compound with it, thus we have chosen NDC for the first time as an oxidant for the kinetics study of active methylene compounds in aqueous acetic acid medium. Oxidation of active methylene compound is also shown by other oxidants like Bromamine-B (BAB)³, peroxomono-phosphoric acid (PMPA)⁴, Ce(IV)⁵, Mn (II)⁶, MnO_4^- ⁷ etc. But good results are obtained

by using NDC in aqueous acetic acid medium.

EXPERIMENT

Active methylene compound employed are commercially available (sigma). All other chemicals used were AnalaR grade. The stock solution of the substrate was prepared in purified glacial acetic acid-water mixture as required. The standard solution of NDC was obtained by dissolving weighed quantity of NDC in 100% acetic acid. The standardization is done iodometrically.

The kinetic measurements were made under pseudo first order condition by maintaining (substrate) \gg (oxidant). The reaction was initiated by adding requisite amount of solution of substrate to the NDC solution containing acetic acid and water

both being equilibrated in a thermostatic bath. The unreacted NDC was estimated iodometrically. The duplicate kinetic runs showed reproducible results of rate constant within $\pm 2\%$.

RESULT AND DISCUSSION

The stoichiometric data established that for complete oxidation of 3 moles of each active methylene compound and one mole of NDC is required. The product of the oxidation was ascertained by the formation of 2, 4-diphenyl hydrazone (DNP) using 2, 4-dinitrophenyl hydrazine⁸. The kinetic data have been collected for 5 fold concentration of oxidant (NDC) at fixed concentration of other reactants and temperature. The linear plot of $\log a/(a-x)$ vs. time shows the first-order rate dependency with respect to NDC.

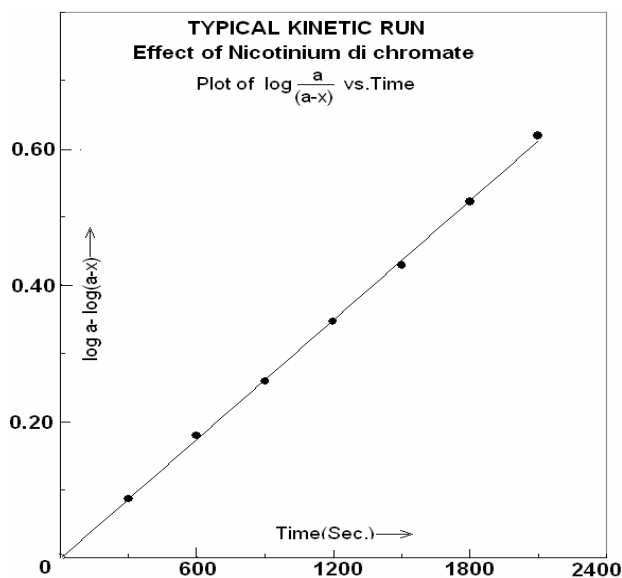


Fig. 1 : $[A.A.] = 1.25 \times 10^{-2} \text{ (mol.dm}^{-3}\text{)}$, $[NDC] = 2.50 \times 10^{-3} \text{ (mol.dm}^{-3}\text{)}$,
 $[H^+] = 1.25 \times 10^{-3} \text{ (mol.dm}^{-3}\text{)}$, HOAc-H₂O = 15 % (v/V), Temp. = 308 K

Table: 1 Typical kinetic run for the effect of Nicotinium dichromate

Kinetics of oxidation reaction between acetyl acetone with NDC
 [A.A.] = 1.25×10^{-2} (mol.dm⁻³), [NDC] = 2.50×10^{-3} (mol.dm⁻³),
 [H⁺] = 1.25×10^{-3} (mol.dm⁻³), HOAc-H₂O = 15 % (v/V)
 Temp. = 308 °K.

| S.No. | Time (sec.) | Vol. of N / 1000 hypo ml. | 10 ⁴ k ₁ (s ⁻¹) |
|-------|-------------|---------------------------|---|
| 1. | 0 | 5.00 | - |
| 2. | 420 | 4.10 | 4.725 |
| 3. | 840 | 3.35 | 4.768 |
| 4. | 1260 | 2.80 | 4.602 |
| 5. | 1680 | 2.30 | 4.623 |
| 6. | 2100 | 1.85 | 4.735 |
| 7. | 2520 | 1.55 | 4.648 |
| 8. | 2940 | 1.25 | 4.716 |

Average k₁ = 4.682×10^{-4} (s⁻¹)
 Graphical k₁ = 4.747×10^{-4} (s⁻¹)

The reaction follows first-order kinetics with respect to substrate at lower concentration and tends toward zero-order at higher concentration. The evidence indicates the formation of complex during the reaction between each substrate and oxidant. The plot

of k₁ vs. [H₂SO₄] was linear with the positive unit slope and passing through origin which led to the conclusion that reaction is fully acid catalyzed and first-order with respect to acid concentration Fig. II.

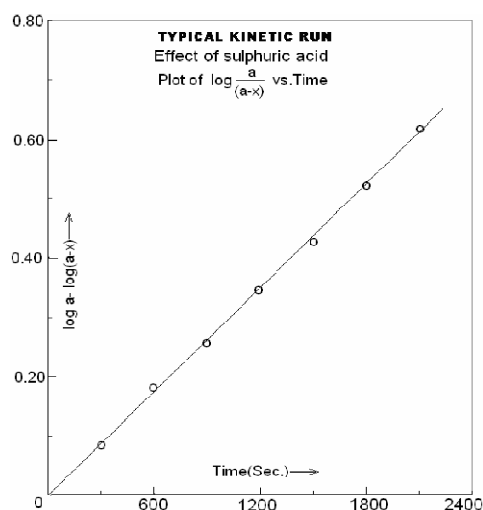
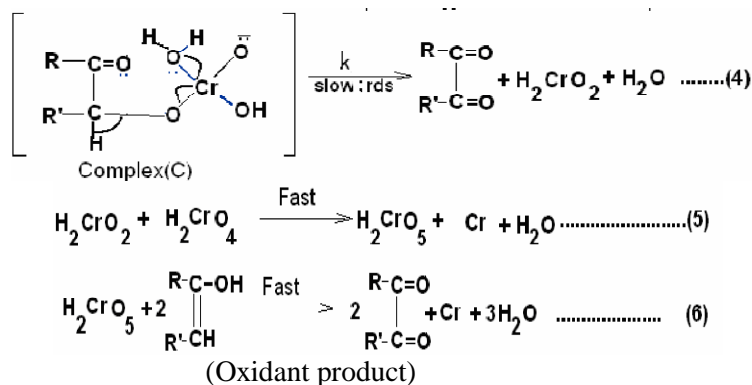


Fig. II: [A.A.] = 1.25×10^{-2} (mol.dm⁻³), [NDC] = 2.50×10^{-3} (mol.dm⁻³),
 [H⁺] = 2.00×10^{-3} (mol.dm⁻³), HOAc-H₂O = 15 % (v/V), Temp. = 308 °K.

$$[\text{H}^+] = 2.00 \times 10^{-3} \text{ (mol.dm}^{-3}\text{)}, \text{HOAc-H}_2\text{O} = 15 \text{ \% (v/V)}, \text{Temp.} = 308\text{K}$$



Where,

R and R' = -CH₃ for Acetyl acetone; R = -C₆H₅ and R' = -CH₃ for Benzoyl acetone;

R = -CH₂NO₂ and R' = -CH₃ for Nitro acetyl acetone.

The above mechanism leads to the following rate law.

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{NDC}]_{\text{T}}} = \frac{k_1 k_2 k [\text{Enol}] [\text{H}^+]}{[\text{Nicotinic acid}] k_1 + k_1 [\text{H}^+] + k_1 k_2 [\text{Enol}] + [\text{H}^+]}$$

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